http://www.e-journals.net

ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
Vol. 4, No.1, pp103-108, January 2007

Application of Activated Carbon for Removal of Arsenic Ions from Aqueous Solutions

R .ANSARI* and M. SADEGH

Chemistry Department, Guilan University, Rasht, Iran
POB 41335-1914, E mail: ransari@guilan.ac.ir

Received 26 August 2006; Accepted 3 October 2006

Abstract The activated carbon (AC) was used for removal of As(III) and As(V) ions from aqueous solutions. Sorption experiments were conducted using both batch and column systems. The effect of some important parameters on sorption of these by AC was studied. It was found that among the different factors affecting sorption capacity and efficiency in removal of arsenic from aqueous solutions, the effect of pH and the oxidation state were the most prominent. The optimum pH values for removal of As(III) and As(V) from aqueous solutions using AC was found 12 and 3 respectively. Impregnation of AC with sulphur contain organic dyes, it is possible to improve As(III) uptake considerably.

Keywords: Removal, adsorption, arsenic, activated carbon

Introduction

Arsenic has been recognized to have an adverse human health hazards and is known to cause cancer in humans in high concentrations. Different levels of toxicity for various arsenic compounds (organic and inorganic) have been reported by some investigators [1-3]. Exposure to arsenic can cause a variety of adverse health effects. Living organisms are exposed to the toxic arsenic species primarily from food and water. However, there is also some scientific evidence that suggests arsenic is a necessary part of the diet. The toxicity of arsenic arises from its ability to react with the sulphydryl groups of the enzyme system thereby blocking the action of the thiol groups of enzymes. Inorganic arsenic is more toxic than its organic compound.

It predominates in drinking water and is present as arsenite [(As (III)] and arsenate [As(V)] depending on pH and redox conditions[2,3].

Among the different oxidation states, because of the ability to complex with certain co-enzymes, arsenite, As (III) is more toxic to animal and plants than As(V) (~10 times) and methylated species (~70 times). The major sources of arsenic in natural waters are also from its widespread use in herbicides, pesticides, fungicides, insecticides, wood preservative, glass manufacturing and electronic industries[2]. Several technologies such as reverse osmosis, ion exchange, adsorption, and adsorbents for removal of arsenic from aqueous solutions have been introduced by many researchers [3-14]. For removal of arsenic from water since As(V) is more efficiently removed than As(III), so pre-oxidation of As(III) to As(V) is mandatory for high arsenic removal from drinking water supplies containing high concentration of As(III). Activated carbon has been recognized a strong and popular adsorbent for elimination of a broad range of impurities or hazardous materials such as aromatic compounds, heavy metal ions, and etc. from aqueous solutions [15-20]. Adsorption is a physical phenomenon, depending largely upon surface area and pore volume. AC is a highly porous material possessing surface area of 300 - 2500 m^2/g. Its large number of very fine pores (micropores) gives it a large inner surface, which is the basis of its remarkable adsorption properties. Due to its more hydrophobic nature its main application is removal of organic contaminations with relatively high MW such as dyes and colors from aqueous solutions. AC is less efficiently applied for removal of simple inorganic metallic ions or small size anions. However this paper deals with its possible application for removal of inorganic arsenic in water which exists more usually as anionic form.

Experimental

The entire chemicals used were of AR grade. A stock As(III) and As(V) solutions (100mg/L) were prepared from As_2O_3 and As_2O_5 in distilled water. Two commercial grades of activated carbon (Merck) as powdered and granulated forms were used in this research. Sorption experiments were carried out using both batch and column systems at RT. In the case of powdered activated carbon (PAC) a batch system and in the case of granulated activated carbon (GAC) a column system were used for adsorption experiment. Column experiments were carried out using a glass tube (1cm × 10cm). The analysis of As(III) and As(V) were carried out using coulometeric titration and Iodometery methods respectively. In coulometric titration, the end point was detected with high precision employing potentiometrically employing Pt and Ag/AgCl in KCl 3M as indicator and reference electrodes respectively. The other more precise determination of arsenic species at very low concentrations (PPb) has been reviewed by Kumaresan [2,3]. All results reported in this paper are the average of at least triplicate measurements and the maximum expected error was ± %5. The details of the procedures can be found in analytical chemistry text books. The Percentage of sorption was calculated using the relationship:

$$\% \text{ Sorption} = \frac{A_i - A_f}{A_f} \times 100$$

Where A_i and A_f are initial (inlet) and final (outlet or effluent) concentrations of arsenic and then the amount of sorption per unit mass of sorbent (x/m) was calculated using the relationship:

$$\frac{X}{m} = \frac{A_i - A_f}{A_f} \times \frac{V}{m}$$

Where V is the volume of adsorbate (cm^3) and m is the amount of adsorbent(g). For further investigation of the data, adsorption isotherms using Langmuir and Freundlich were also used.

Results and Discussion

Effect of pH

The adsorption of arsenic from aqueous solution using activated carbon in this research was found to be a highly pH dependent process. pH of solution, in fact determines the chemistry and speciation of arsenic ions and also affects the surface charge of the adsorbent. In this experiment, the adsorption behaviour of As(III) and As(V) ions was studied at different pH values, using 1.0 g of AC and a fixed amount of arsenic. The results obtained are shown in Table 1 which shows that adsorption or removal of As(III) ions increases with increasing the pH.

Table 1 Influence of pH on the adsorption of arsenic (III) on to the AC (column system)

pH	2	7	10	12
% sorption	10	55	77	90

*Adsorbent = 1.0 g of activated carbon (granulated form),
Adsorbate= 10 mL of 25 ppm, Flow rate = 2 mL min^{-1}.

The same experiments were performed for arsenic (V) and the results obtained have been shown in Table 2. As our data show, powdered form of AC is more efficient than granulated form due to its higher surface area.

Table 2 Influence of pH on the adsorption of arsenic (V) on to AC

pH	3	7	10
% Sorption (GAC)*	60	55	40
% Sorption (PAC)	75	70	60

*All conditions were the same as used for As(III) in Table 1.
GAC= Granulated Activated carbon, and
PAC= powdered Activated carbon.

It is interesting to note that adsorption of arsenic by AC is very dependent on the oxidation state. As(III) and As(V) are more efficiently adsorbed by AC at basic and acidic conditions respectively. In aqueous solutions, arsenic (V) exhibits anionic behavior; within a pH range of 2-11, it is replaced by $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}. The removal of As(V) by AC is supposed to be carried out via anion exchange mechanism as well as physiochemical adsorption due to the highly porous structure of AC. The surface of the AC is positively charged under acidic conditions, and then these positive charges are balanced with their accompanying anions. So, these anions can be exchanged with the other anionic species present in the solution.

Effect of concentration of adsorbate

The effect of arsenic concentration on the adsorption was studied under optimized pH found from our previous results. Concentrations of As(III) and As)V) varied from 20-150 ppm. 10 mL of each concentration of arsenic was treated with the adsorbent at pH value of 12. The results are depicted in Table 3 which show AC is more efficient adsorbent at low concentrations of arsenic. Decrease in sorption percentage at higher concentrations might be due to the relatively smaller numbers of active sites available at higher arsenic concentrations.With increasing of the initial concentration of arsenic total amount of arsenic removal (X/m) is increased.

Table 3 Effect of initial As(III) ion concentration on sorption using activated carbon

Concentration ppm	10	20	50	100	150
% Sorption , As(III) pH=12	95	92	85	75	66
% Sorption , As(V) pH= 3	84	75	60	45	30

The adsorption data for arsenic were also further analyzed by means of the Langmuir and Freundlich isotherm models (Table 3). Langmuir and Fruendlich equations can be shown as $1 / X = 1 / X_m + 1 / bC_e$), $X / m = KC_e^{1/n}$ (or $\log X/m = \log K + 1/n \log C_e$) respectively[21]. Where C_e is the equilibrium concentration of Cr(VI) solution (mg/L), X is the amount sorbed by activated carbon (mg/g), X_m is the maximum amount sorbed, b a Langmuir's constant signifying energy of sorption, K and n are Fruendlich's constants indicating sorption capacity and intensity, respectively.

Table 4 Effect of the initial concentration of As(III) ion on adsorption parameters using Freundlich and Langmuir equations

Conce. of As(III) ppm	%Ads	X/m mg/g	Ce ppm	1/Ce	logX/m	logCe	m/X
20	92	184.0	1/6	0.625	1.26	0.20	5.4
50	85	445.0	6	0.16	1.6	0.77	2.24
100	75	750.	25	0.04	1.87	1.39	1.33
150	66	0.99	51	0.02	1.99	1.7	1.01

The analysis of the data obtained for As(III) sorption showed that they fit better with the linearized form of Langmuir equation (Figure 1). In the case of As(V) sorption, the data obtained showed that they fit better with the Freundlich adsorption isotherm equation (linearized form).

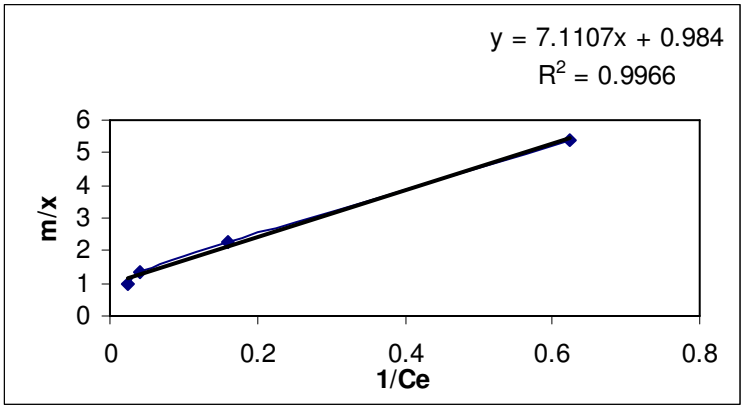

Figure 1 Adsorption isotherm obtained form As(III) sorption by AC using Langmuir equation (linearised form)

Effect of impregnation or pre-treatment of AC and modified AC on As(III) removal

In this experiment fixed amounts of AC (1.0 g) as both granulated and powdered forms were treated with 50 mL of 0.01 M some selected salts: $FeSO_4$, $Fe(NH_4)(SO_4)_2$, $AgNO_3$, $CuSO_4$ for 30 min. Then the sorbents were washed with copious distilled water in order to complete removal of the loosely adsorbed salts on the surface before running the adsorption experiments. 10.0 mL of arsenic solution with concentration of 50 ppm used for running each experiment. The pH value for As(III) adsorption was selected at 12 using 0.01M NaOH solution. Shaking time for batch experiment in the case of PAC was 1h at RT and the weight of sorbent was chosen 0.50 g. In this part of our investigation, we also treated AC with some commercial sulphur containing organic dyes, then examined them for removal of As(III).

Pretreatment of AC with S-contain compounds was carried out with treatment of 1.0 g AC and 50 mL of 500 ppm dyes for 30 min. The modified AC washed with enough distilled water before adsorption of arsenic. In the case of AC impregnated with the selected dyes, 50 mL of arsenic solution with concentration of 100 ppm was used. It was because of their higher sorption capacity. The results obtained have been summarized in Table 5.

Table 5. Influence of pretreatment of AC on uptake of As(III) ion

Adsorbent	% Sorption	Adsorbent	% Sorption	Adsorbent*	% Sorption
GAC	78	PAC	90	PAC	90
GAC-Fe(III)	70	PAC-Fe(III)	85	PAC-DZ	95
GAC-Fe(II)	80	PAC-Fe(II)	-	PAC-H.Y	97
GAC-Cu^{2+}	85	PAC-Cu^{2+}	96	PAC-H.G	95
GAC-Ag^{+}	85	PAC-Ag^{+}	97	PAC-M.B	97

*DZ= Dithizone (Diphenyl thiocarbazone), H.Y.= Hydrozol yellow, H.G= Hydrozol green, MB=methylene blue.

As it has been indicated (table 4) impregnation of AC with copper or silver salts leads to some improvement in uptake of As(III) from aqueous solutions but the Fe(II) and Fe(III) salts leads to some diminish in As(III) removal. Considerable improvement in arsenic removal was observed when AC impregnated with S- containing compounds was used. This can be due to the high tendency of arsenic to bond with sulphur.

Adsorption of As(V) ions using AC with and without modifications

In this part of our studies, 0.50 g of adsorbent (PAC and impregnated PAC) used for As(V) removal from a synthetic test solution (10 mL of 50 ppm). The experiment was carried out in two different pH values at RT. Shaking time was selected 1h at RT. As our results obtained in this research show, activated carbon is a more efficient adsorbent for As(V) removal in basic conditions. Pre-treatment of AC with Fe(III), Cu(II) and silver salts improves uptake of the AC for arsenic (V) from aqueous solutions. This can be due to the formation of stable and insoluble compounds of these metals with arsenate or arsenic (V) anion. It has also been reported by the previous researchers [10], that a relatively new and promising method for reducing arsenic levels (both trivalent and pentavalent) in drinking water is the use of iron oxide filters. As our results in this paper show (Table 6), pretreatment of AC with organic sulphur containing dyes do not result any improvement in As(V) uptake. Rather, some decrease was observed. As(V) in contrast to As(III) do not react with sulphur containing organic compounds.

Table 6 Influence of pretreatment of AC on uptake of As(V) ions at two different pH

Adsorbent	PAC/Fe^{3+}		PAC/Cu^{2+}		PAC/Ag^{+}		PAC/DZ		PAC/HY		PAC/HG		PAC/mb		PAC	
pH	3	10	3	10	3	10	3	10	3	10	3	10	3	10	3	10
% Sorption	80	90	85	97	85	95	66	50	60	45	60	45	66	50	75	60

Conclusion

Activated carbon as powdered or granulated forms can be used for effective removal of As(III) and AS(V) ions from aqueous solutions. The amount of arsenic uptake by AC is greatly dependent on pH and its oxidation state. Adsorption of arsenic by AC can be improved by impregnation of AC employing suitable chemicals (e.g. sulphur contain textile dyes for As(III) and Fe(III) salts for removal of AS(V) from aqueous solutions.

Acknowledgment

The authors are grateful for the financial support of this project by the Research Council of Guilan University, Rasht, Iran.

References

1. Squibb K S and Fowler B A, *Biological and Environmental Effects of Arsenic*, Elsevier, Amsterdam, 1983, 233
2. Kumaresan M and Riyazuddin P, *Current Science*, 2001**, 80 (7),** 837
3. Dang Q, Hung, Olga Nekrassova and Richard G Compton, *Talanta*, 2004, **64**, 269
4. Ahmed. F, Jalil M A, Ali M A, Hossain M D and Badruzzaman A B M M F Ahmed (Ed.), Bangladesh Poribesh Andolon, 2000, 177
5. Chen H W, Frey M M, Clifford D, McNeill L S and Edwards M, 1999, **91(3),** 74
6. Cheng C R, Liang S Wang H C and Beuhler M D , 1994, **86(9),** 79
7. Ahmed F**,** *Technolgies for arsenic removal from Drinking water*" 2000, 251
8. Hering J G, Chen P Y, Wilkie J A, Elimelech M and Liang S, *J. American Water Works Association*, 1996, **88(4),** 155
9. Hering J G, Chen P, Wilkie J A, Elimelech M, *J. Env. Eng., ASCE,* 1997, **123(8)**, 800
10. Joshi A and Chaudhury M, *ASCE Journal of Environmental Engineering*, 1996, **122(8),** 769
11. Kartinen E O and Martin C J, *J. Desalination*, 1995**, 103**, 79
12. Pierce M L and Moore C B, *Water Resources*, 1996, **16**, 1247
13. Shen Y S, *J. American Water Works Association*, 1973, **65(8)**, 543
14. Khalid N, Ahmad S, Toheed A and Ahmed J, *Adsorption Sci. and Technology*, 1998, **16(8),** 655
15. Ansari R and Masoudi M, *Inter. J. of Chemistry*, 2004, **14(3)**, 139 .
16. Ansari R and Nikravan S S, *Int. J. of Chemistry* , 2005**, 15 (2),** 95
17. Ansari R, *Arab World Water Journal (AWW)*, 2004, 10
18. Ansari R and Omidvari R, *Polish Journal of Environmental Studies*, 2005, **14 (2)**, 191
19. Gomez V and Serrano Macias-Garcia A, *Water Res* . 1998, **32 (1)**, 1
20. Guo-hua Xiu and Ping Li*, Carbon*, 2000, **38**, 975
21. Lee C K, Low K S and Kek K L, *Biores. Technol*.,1995, **54**, 183